



Removal of priority and emerging pollutants from aqueous media by adsorption onto synthetic organo-functionalized high-charge swelling micas



Julia Martín^{a,*}, María del Mar Orta^b, Santiago Medina-Carrasco^c, Juan Luis Santos^a, Irene Aparicio^a, Esteban Alonso^a

^a Department of Analytical Chemistry, Escuela Politécnica Superior, University of Seville, E-41011 Seville, Spain

^b Department of Analytical Chemistry, Faculty of Pharmacy, University of Seville, E-41012 Seville, Spain

^c X-Ray Laboratory (CITIUS), University of Seville, E-41012 Seville, Spain

ARTICLE INFO

Keywords:

Emerging pollutants
High-charge swelling micas
Organic functionalization
Water samples
Removal

ABSTRACT

In this work, the removal of different types of emerging pollutants (four perfluoroalkyl compounds, two preservatives, three surfactants and nine pharmaceutical compounds) from aqueous solution by adsorption onto two novel synthetic clays, a high-charge swelling mica (Na-Mica-4) and an organo-functionalized mica (C₁₈-Mica-4), was evaluated. Na-Mica-4 and C₁₈-Mica-4 were prepared and characterized by X-Ray diffraction, Zeta potential, specific surface area, thermogravimetric analysis and transmission electron microscopy, before and after adsorption experiments.

The influence of the aqueous sample pH, salt addition and extraction time in the removal were evaluated. The results showed the high adsorption affinity of C₁₈-Mica-4 for most of the emerging pollutants analysed after a removal time of 24 h (14 out of 18 pollutants were effectively removed [70–100%]). A high correlation was observed between the log K_{ow} of the selected emerging pollutants and the adsorption onto C₁₈-Mica-4. The results also indicate that adsorption occurs in the interlayer space. While the removal rates with Na-Mica-4 were in the range 8–97% after seven days, some of the compounds, perfluorobutanoic acid and most of pharmaceutically active compounds, were not adsorbed onto the high-charge mica. C₁₈-Mica-4 was effectively used for the removal of contaminants from four types of water samples.

1. Introduction

Preservation and improvement of water quality is paramount to keep the health and sustainability of the different ecosystems. The occurrence of natural or anthropogenic contaminants of emerging concern at levels between ng L⁻¹ and µg L⁻¹ has been reported in many publications including pesticides, industrial compounds, pharmaceuticals and personal care products, among others (Ruhí et al., 2016; Rodil et al., 2012; Bolong et al., 2009; Caliman and Gavrilescu, 2009). Conventional urban wastewater treatment plants (WWTPs) are not specifically designed to remove residual concentrations of organic compounds. Ultraviolet lamps have been used mainly for disinfection, while alternative technologies including advanced oxidation processes (such as ozonation with H₂O₂ and the use of Uv/H₂O₂), nanofiltration, reverse osmosis, and adsorption (Carmalin and Eder, 2018; Capodaglio, 2017; Grassi et al., 2012; Katsoyiannis et al., 2011; Liu et al., 2009), have been investigated but most of them hardly implemented as tertiary treatment in WWTPs.

Adsorption is one of the alternatives for the removal of emerging pollutants due to its high efficiency, selectivity, low cost, simplicity and the possibility of reusing and recycling the adsorbent (Carmalin and Eder, 2018; Martins et al., 2017; Méndez et al., 2017; Tapia-Orozco et al., 2016; Rashed, 2013; Park et al., 2011). The suitability of an adsorbent is determined by properties such as surface area, mechanical stability or pore size. Activated carbon (AC) is the most widespread adsorbent for the removal of organic pollutants because of its microporosity, which ensures good sorption capacities (Rigobello et al., 2013; Djilani et al., 2012; Ruiz et al., 2010; Yu et al., 2008; Nevskaja and Guerrero-Ruiz, 2001). However, the use of ACs is costly because only a percentage of carbons can be reused after the adsorption process (Sharma and Wankat, 2010), usually no more than 40% (Wang and Balasubramanian, 2009). Moreover, thermal regeneration of activated carbons has been explored for emerging pollutants removal from effluent wastewater (Marques et al., 2017) but it was observed that the regenerated activated carbon was not as efficient as new activated carbon. Therefore, alternative sorbents are desirable to overcome these

* Corresponding author.

E-mail address: jbueno@us.es (J. Martín).

drawbacks (Orta et al., 2018; Suna et al., 2017; Pazos et al., 2017). In this context, clay minerals have attracted much attention owing to their high cation exchange, swelling properties, and high surface areas (Lingya et al., 2016; Alba et al., 2009; Sánchez-Martín et al., 2008; Zadaka et al., 2007; Lagally, 2001).

Compared to other clay minerals like smectites or vermiculites, micas exhibit higher layer charge density. Naturally occurring micas do not swell in water and ion-exchange reactions with the interlayer cations would be extremely slow process (Kodama et al., 2000). In contrast, the synthetic highly charged mica Na-mica-4 has an unusual swelling behaviour and selective cation exchange properties, which may become potentially useful for hazardous cation separations from solutions (Alba et al., 2006; Park et al., 2002).

In addition, clay minerals can be modified in order to enhance their removal efficiency in aqueous media. The organo-functionalization of their surface allows for the effective sorption of non-ionic pollutants in the interface. The sorption of organic micropollutants by organoclays depends on the structure and size of alkylammonium ions, type of clay, cation exchange capacity, density and orientation of the alkyl chains on the surface, and features such as solute size, shape and relative solubility/hydrophobicity (Pazos et al., 2017; Alba et al., 2011a). C18-mica prepared by a cation-exchange reaction between Na-mica-4 and primary alkylamine shows better expandability and structural properties than native Na-mica-4, improving its adsorption capacity (Pazos et al., 2012; Alba et al., 2011a). Up to now, few studies have examined the use of C18-Mica-4 as adsorbents for the retention of organic pollutants. Among them, Pazos et al. (2017) and Alba et al. (2011a) studied the adsorption of some pollutants from petroleum refineries such as benzene, toluene and phenol on these materials. More recently Orta et al. (2018) evaluated Na-Mica-4 and C18-Mica-4 for the removal of linear alkylbenzene sulfonates (LAS) from aqueous samples. More studies are required to extend the use of this promising mica for the removal of other families of organic compounds.

In the present work, the adsorption of Na-Mica-4 and C₁₈-Mica-4 is evaluated for the removal of eighteen micropollutants including priority substances (Directive, 2013/39/EU, 2013), substances of the last watch list (Decision 2015/495/EU) and contaminants of emerging concern: two groups of industrial compounds (surfactants and perfluoroalkyl compounds), personal care products (preservatives), and multi-class pharmaceuticals (anti-inflammatory drugs, antibiotics, anti-epileptic drugs, β -blockers, nervous system stimulants and lipid regulators).

2. Materials and methods

2.1. Materials and reagents

SiO₂ (Sigma Aldrich; CAS no. 112945–52-5, 99.8% purity), Al(OH)₃ (Sigma Aldrich; CAS no. 21645-51-2), MgF₂ (Sigma Aldrich; CAS no. 7783-40-6), and NaCl (Sigma Aldrich; CAS no. 7647-14-5, \geq 99.5% purity) were purchased from Sigma-Aldrich for the synthesis of Na-Mica-4. Primary alkylamine octadecylamine salt (CAS no. 124-30-1, \geq 99.0% purity) was purchased from Sigma Aldrich for the organo-functionalization of Na-Mica-4.

HPLC-grade acetonitrile (ACN), methanol (MeOH) and water were supplied by Romil Ltd. (Barcelona, Spain).

Hydrochloric acid, sodium hydroxide, sodium chloride (NaCl), and formic acid were obtained from Panreac (Barcelona, Spain). Ammonium formate and ammonium acetate were purchased from Sigma-Aldrich (Steinheim, Germany). All of them were analytical grade.

High purity standards of perfluorobutanoic acid (PFBuA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), 4-nonylphenol (NP), methylparaben (MeP), and propylparaben (PrP) were supplied from Sigma-Aldrich (Steinheim, Germany). Sodium dodecylsulfate (AS-C12) and sodium

Table 1

Acronym and physico-chemical properties of the selected pollutants.

Compound	Acronym	pKa	Log K _{ow}
Methylparaben	MeP	8.3	1.7
Propylparaben	PrP	8.2	2.6
Perfluorobutanoic acid	PFBuA	0.2–0.4	2.4
Perfluoroheptanoic acid	PFHpA	–	5.3
Perfluorooctanoic acid	PFOA	2.8	6.3
Perfluorooctane sulfonic acid	PFOS	– 3.3	4.1
Nonylphenol	NP	10.7	4.5
Dodecyl sulfate	AS C12	< 1	2.4
Octadecyl sulfate	AS C18	< 1	2.6
Diclofenac	DIC	4.1	4
Ibuprofen	IBU	4.4	3.8
Salicylic acid	SAL	3.5	2.3
Trimethoprim	TRI	6.6	1.4
Carbamazepine	CAR	13.9	2.3–2.5
Propranolol	PRO	9.5	0.7
Caffeine	CAF	14	– 0.1
Clofibrac acid	CLOF	2.5–3.2	2.6
Gemfibrozil	GEM	4.7	4.8

octadecylsulfate (AS-C18) were supplied by Alfa Aesar (Barcelona, Spain). Diclofenac (DIC), ibuprofen (IBU), salicylic acid (SAL), trimethoprim (TRI), carbamazepine (CAR), propranolol (PRO), caffeine (CAF), clofibrac acid (CLOF), and gemfibrozil (GEM) were purchased from Dr. Ehrenstorfer (Augsburg, Germany).

Individual stock standard solutions of each compound were prepared in methanol and stored at 4 °C. Mixtures of the studied compounds at different concentration levels were prepared freshly before each experiment by dilution of the stock standard solutions in a mixture methanol: water (50:50, v/v). The acronym, pK_a and log K_{ow} of each analyte are shown in Table 1.

2.2. Synthesis of swelling high charged micas

Na-Mica-4 was synthesized by the NaCl melt method following a procedure described by Alba et al. (2006). Its cation exchange capacity (CEC) is 468 mequiv 100 g⁻¹ and its structural formula is Na₄[Si₄Al₄]Mg₆O₂₀F₄ nH₂O. The starting products employed were SiO₂, Al(OH)₃, MgF₂ and NaCl. The reactants were weighed and mixed in an agate mortar until the mixture was homogeneous.

Heat treatments were carried out in a Pt crucible at 900 °C during 15 h using a heating rate of 10 °C min⁻¹. The product was washed with distilled water, and the solid was separated by filtration, dried at room temperature, and then ground in agate mortar.

2.3. Organo-functionalization of Na-mica-4

The organomica C₁₈-Mica-Na was prepared by a cation-exchange reaction between the mica and an excess of primary octadecylamine (2 CEC of Na-Mica-4) (Alba et al., 2011a). The primary amines were dissolved in an equivalent amount of HCl (0.1 M) and the resulting mixture was stirred for 3 h at 80 °C. The alkylammonium solution was then mixed with 0.6 g of Na-Mica-4 and stirred for 3 h at 80 °C. Deionized water (50 mL at 50 °C) was added and the mixture was stirred for 30 min at 50 °C, and the dispersion was then centrifuged at 8000 rpm for 30 min at 5 °C. The product was dissolved in a hot ethanol: water mixture (1:1) and stirred for 1 h, centrifuged at 8000 rpm for 30 min at 5 °C. Finally, the precipitate was left to dry at room temperature.

2.4. Sample collection

Influent and effluent wastewater collected in September 2016 from a wastewater treatment plant located in Seville (Spain). Six daily-composite samples were obtained by mixing sample volumes collected every hour by an automatic device (Sigma 900 MAX Portable Sampler)

Download English Version:

<https://daneshyari.com/en/article/8868949>

Download Persian Version:

<https://daneshyari.com/article/8868949>

[Daneshyari.com](https://daneshyari.com)